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Decisive intermediates responsible for the carbonaceous products of CO_2 electro-reduction on nitrogen doped sp^2 nanocarbon catalysts in $NaHCO_3$ aqueous electrolyte

Junyuan Xu,[a] Bingsen Zhang,[a] Bolun Wang,[a] KuangHsu Wu,[a] Zhangquan Peng,[b] Qingfeng Li,[c] Gabriele Centi,[d] and Dang Sheng Su*[a]

Abstract: Nitrogen doped sp^2-nanocarbon materials have been considered as promising catalysts for CO_2 electro-reduction. However, fundamental understanding about the product selectivity and the reaction routes is still lacking. In this report, the reaction mechanism on nitrogen doped sp^2-nanocarbon materials is resolved by clarifying the authentic origin of the carbonaceous products: CO and HCO_2^-. Two carbon-reduction pathways are identified base on a series of comparative study using differential electrochemical mass spectrometry and in-situ CO adsorption experiments: a dominant pathway leading to CO from CO_2 and a secondary pathway leading to HCO_2^- from HCO_3^-. Neither hydrocarbon (C_xH_y), nor alcohol or aldehyde ($C_xH_yO_z$) was detected in the reduction of CO_2, however CO which is generally regarded as an intermediate to be transformed into these products on metal catalysts can undoubtedly be produced and adsorbed on nitrogen doped sp^2-nanocarbon catalysts during the reaction.

A promising path to reduce carbon dioxide emissions into the atmosphere is the transformation of carbon dioxide into valuable chemicals through electrochemical means, using renewable energy sources.[1-3] A landmark discovery in this area was made by Hori in 1985, who found that CO_2 can be reduced to CO, HCO_2^-, C_xH_y and $C_xH_yO_z$ on a bulk copper electrode.[4] Later, precious metals (Ag, Au and Pd) and other non-precious transition metals (Sn, Ni and Fe) have received tremendous attention in the field and it was found that the product distribution varied over a broad range with different metals.[2,5]

Recently, nitrogen doped sp^2-nanocarbon (NDSN) materials have emerged as a class of metal-free catalysts with reasonable activity for the electro-reduction of CO_2 (Table S1).[6] The idea behind is exploring the potential of metal-free catalysis for this important reaction. Kumar and co-workers have reported direct conversion of CO_2 to CO over nitrogen doped carbon nanofibers in ionic liquid of 1-ethyl-3-methylimidazolium tetrafluoroborate.[6a] The same conversion was also observed separately by Ajayan et al. and Strasser et al. that CO was the dominant carbonaceous product on nitrogen doped carbon nanotubes (NCNT)[6b,6c] and nitrogen doped porous carbon black[6d] in a 0.1 M $KHCO_3$ solution. However, HCO_2^- was reported as the main product instead of CO using NCNT as catalyst in 0.1 M $KHCO_3$ solution by Zhang et al.[6e] The reason behind such inconsistent product distribution remains unclear and solving it requires insights into the reduction mechanism.

Although a variety of C1 or C2 compounds could be produced from the electro-reduction of CO_2 on metal catalysts(as listed in Table S2), only CO and HCO_2^- could be obtained using NDSN materials as catalysts.[6] Theoretical computation suggested that the absence of C_xH_y or $C_xH_yO_z$ should be ascribed to the poor adsorption capability of CO on NCNT.[6b,6c,7] However, recent theoretical calculation from Guo et al. suggested that *CO adsorbed on strong bonding sites of (6, 0) NCNT could be reduced to HCHO and CH_3OH owing to its high degree of curvature.[8] Unfortunately, there lacks an experimental proof to elucidate the determining factor for the product distribution of NDSN catalysts.

Under realistic situation, however, the reaction system is not as ideal as those described in computational studies. In particular, electrolyte species are involved during the course of CO_2 reduction and their participation should not be ignored. For example, water in the electrolyte not only acts as a proton source for CO_2 reduction but also as a competing reactant for electrons during the cathode process on NDSN and metal catalysts.[2-6] The Faradaic efficiency (FE) of H_2 increased (20-90 %) with raising potentials thus the FE of carbonaceous reduction products was inhibited especially under high potentials. In addition, bicarbonate salt electrolyte has been frequently employed to increase the solubility of CO_2 in aqueous electrolyte (CO_2 has a solubility of 30 mM in pure water at standard ambient temperature and pressure) as a measure to improve the FE of the CO_2 reduction.[2-6,9] In such a case, the presence of relatively concentrated HCO_3^- species (100-500 mM), created another possible origin of the products during the cathode process. Despite that the dissolved CO_2 was generally regarded as the dominant carbon source for electro-reduction,[2-6,9] the possibility of the direct reduction of HCO_3^- species was still in dispute[10] and this matter had been commonly ignored. Previous studies have reported CH_4, C_2H_4, HCHO, CH_3OH and other carbonaceous products on Cu and Pt electrodes[10a] in a bicarbonate electrolyte in the absence of CO_2, and HCO_2^- could be produced from HCO_3^- on Pd impregnated polymer electrodes[10b] or metallic Pd electrodes.[10c] Furthermore, a recent spectroscopy study by Innocent et al. showed that HCO_3^-

[a] Dr. J. Xu, B. Zhang, B. Wang, K. Wu, Prof. D. Su
Shenyang National Laboratory for Materials Science
Institute of Metal Research
Chinese Academy of Sciences
72 Wenhua Road, Shenyang 110016, China
E-mail: dssu@imr.ac.cn
[b] Prof. Z. Peng
State Key Laboratory of Electroanalytical Chemistry
Changchun Institute of Applied Chemistry
Chinese Academy of Sciences
5625 Renmin Road, Changchun 130022, China
[c] Prof. Q. Li
Department of Energy Conversion and Storage
Technical University of Denmark
Kemitorvet 207, DK-2800 Kgs. Lyngby, Denmark
[d] Prof. G. Centi
Department of Electronic Engineering, Industrial Chemistry and Engineering, Section Industrial Chemistry
University of Messina and INSTM/CASPE (Laboratory of Catalysis for Sustainable Production and Energy)
V.le F. Stagno D'Alcontres 31, Messina, 98166, Italy

was the only electroactive species to produce HCO_2^- on Pb electrodes in HCO_3^-/CO_2 solution.[10d] It is important to unravel the decisive intermediates responsible for the carbonaceous product distribution, particularly there is only a few reports paid some attention to this aspect for NDSN catalysts.

The present work aimed to identify the possible reaction routes and mechanism governing the carbonaceous product distribution of CO_2 electro-reduction on NDSN catalysts in HCO_3^-/CO_2 solution. Onion-like carbon (OLC),[11] carbon nanotube (CNT) and graphene were selected as representative sp^2-nanocarbon materials for the investigation. Ammonia post-treatment was conducted to introduce nitrogen species into the carbon framework.[12] The N-doped nanocarbons were referred as NOLC, NCNT and NG, respectively. The structural details and metal residuals were provided in the supporting information, (Figures S1, S2, Tables S3 and S4). By combining differential electrochemical mass spectrometry (DEMS)[13] and a series of in-situ CO adsorption experiments, we are able to unravel the authentic carbon source of the formed CO and HCO_2^- during CO_2 electro-reduction on NDSN catalysts in HCO_3^-/CO_2 solution.

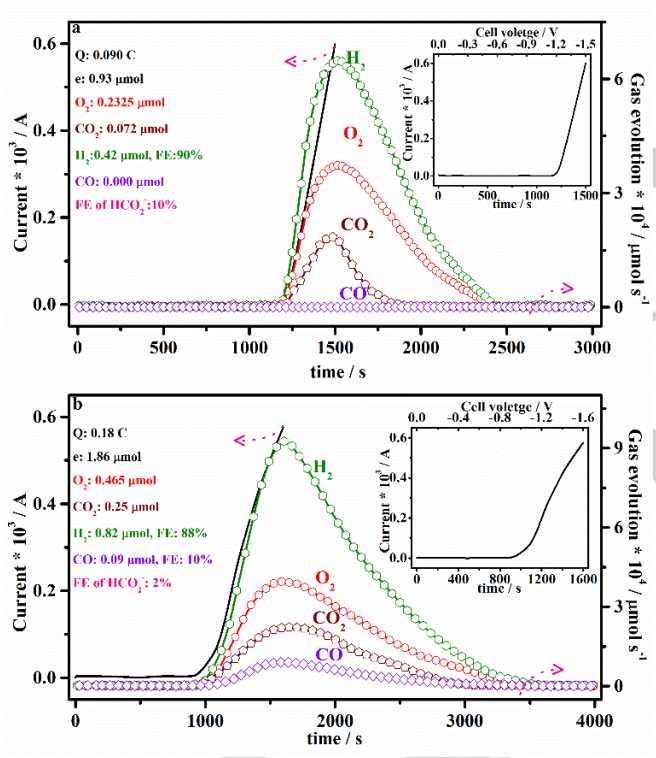

Figure 1. Normalized DEMS characterization (loading gas, Ar, 1 mL min^{-1}) of oxidized CNT (OCNT, a) and NCNT-1 (b) in Ar saturated $NaHCO_3$ electrolyte at 25 °C. The insert was the corresponding electrochemical data (scan rate, 1 mV s^{-1}).

First of all, the product distribution and FE of each product were examined using potential-controlled electrolysis, which was performed in a 0.5 M $NaHCO_3/CO_2$ electrolyte at ambient temperature. For the investigated NDSN catalysts, CO (Figure S3a) was the major product detected by an online gas chromatography. Only a trace amount of HCO_2^- with a FE in the range of 0.2-3 % was detected by ^1H nuclear magnetic resonance (NMR) (Figures S3b and S3c). Neither hydrocarbon (C_xH_y) nor alcohol/aldehyde ($C_xH_yO_z$) was detected, even at an applied potential higher than -2.0 V *vs* Reversible Hydrogen Electrode (RHE). This result with CO as the major product was consistent with the previous literature,[6a-6d] except for the result from Zhang et al.[6e] Specially, it should be noted that the normalized activity for CO production for all the NDSN catalysts should be an integrated result of the nitrogen content, conductivity and electroactive surface area of catalysts (Figures S4 and S5).

Since the selectivity cannot be simply tuned by modulating the morphology of sp^2 carbon framework or the composition of nitrogen species, our attention was shifted to the intermediates derived from the reduction of possible carbon sources. It has been pointed out that the carbonaceous products could either come from the fed CO_2 or the HCO_3^- in the electrolyte,[10] the authentic source of reduction products (particularly CO and HCO_2^-) was still unclear. Hence, we employed DEMS to in-situ quantify the gas products without supplying CO_2. For oxidized CNT (OCNT), after the reaction occurred at -1.1 V (1100 s), the amount of gas products (without any CO) increased until the reaction ended at -1.5 V (1500 s, Figure 1a). The delayed gas signal (which ended at about 2500 s) was due to the slow diffusion of gas products to the detector in mass spectrometer. In view of the e^-/O_2 ratio (4, (0.93 μmol)/(0.2325 μmol)), it can be concluded that O_2 was the only oxidation product, which was generated from the water splitting ($2H_2O \rightarrow 4H^+ + 4e^- + O_2$) at the anode. The detected CO_2 signal indicated that the HCO_3^- could decompose to CO_2 at a slow rate of 1.8×10^{-4} μmol s^{-1} ((0.072 μmol)/(400 s)). Two possible reaction pathways ($HCO_3^- \rightarrow CO_2 + OH^-$; $HCO_3^- + H^+ \rightarrow CO_2 + H_2O$) might take place at the same time.[14] In addition, H_2 ($2H^+ + 2e^- \rightarrow H_2$) was collected at the cathode. The value of the e^-/H_2 ratio (2.21, (0.93 μmol)/(0.42 μmol)) was higher than 2.0, which indicated that a part of the electrons was consumed by the reduction of carbonaceous species into products other than CO. This agreed with the well-known fact that OCNT or undoped CNT cannot promote the conversion of CO2 to CO.[6] The electrolyte was analyzed using ^1H NMR after the reaction, and HCO_2^- was the only detectable carbonaceous product.

In contrast to OCNT, CO was detected during the reduction with NCNT as the catalyst (Figure 1b). This indicated that the doped nitrogen could promote the reduction of CO_2 generated from the decomposition of HCO_3^-. This was supported by the much higher decomposition rate of HCO_3^- (4.8×10^{-4} μmol s^{-1}, ((0.25+0.09 μmol)/(700 s)) vs 1.8×10^{-4} μmol s^{-1} in OCNT) as the conversion of CO_2 to CO may accelerate the decomposition of HCO_3^-. Considering the lower ratio of $e^-/(H_2 + CO)$ (2.04, (1.86 μmol)/(0.09 μmol)), it was reasonable that fewer HCO_2^- was produced since less electrons left after they were consumed by the reduction to H_2 and CO at the cathode.

In addition, the FE for CO production in $NaHCO_3$/Ar electrolyte (Figure 1b) was much lower than that in the $NaHCO_3/CO_2$ solution (Figure S3a), whereas the FE of HCO_2^- in Ar was slightly higher (Figures 1b and S3c). This suggested that the CO_2 fed from outside should be the main origin of CO. The increased FE of CO should be ascribed to the abundance of the fed CO_2 which could not be achieved by the slow decomposition rate of HCO_3^-.[15] Moreover, the increased CO_2 (of weak acidity) concentration can

suppress the adsorption of HCO_3^- (of weak basicity) to the NCNT (of weak basicity) and thus the FE of HCO_2^- decreased.[6e] Ultimately, the carbon-reduction pathway was validated by an electrolysis experiment (Figure S6) in the H_2O/CO_2 electrolyte where the concentration of HCO_3^- could be negligible and only CO was obtained without any HCO_2^-.

It was clear that HCO_2^- could be reduced from HCO_3^- in absence of CO related intermediates, and vice versa, HCO_2^- could not be produced without HCO_3^- while CO was generated from CO_2. These results suggested that HCO_3^- should be the true source of HCO_2^-, rather than other intermediates relating to the CO generated by CO_2 reduction. This conclusion was consistent with the in-situ reflectance spectroscopy result in the literature.[10d] Moreover, it was more reasonable that HCO_2^- did not originate from the CO related intermediates, otherwise it should also be feasible to produce other carbonaceous reduction products (C_xH_y or $C_xH_yO_z$) besides HCO_2^- by the further reduction of adsorbed CO. In fact, no other carbonaceous reduction product (C_xH_y or $C_xH_yO_z$) was observed apart from CO and HCO_2^- in this study.

In case of the electro-reduction of CO_2 on metal surface, it has been proposed that the product distribution of CO_2 reduction depends on the binding energy of CO to electrode surface.[16] Metals that adsorb CO weakly such as Zn, Au and Ag (Table S5) could only produce CO, as CO can easily desorb from the surface before it can be further reduced to C_xH_y or $C_xH_yO_z$. This was also supposed as the reason of why C_xHy or $C_xH_yO_z$ was hardly generated on NDSN catalysts (Table S5).[6b,6c,7] However, recent studies showed that C_xH_y or $C_xH_yO_z$ could be produced on Zn, Au and Ag at high potentials (after -1.0 V *vs* RHE).[17,18] Therefore, the high binding energy of CO may not be indispensable for the formation of C_xH_y or $C_xH_yO_z$. This suggested that producing C_xH_y or $C_xH_yO_z$ on NDSN catalysts may be possible under a specific condition in spite of their low CO adsorption capability.

A series of CO adsorption experiments were conducted to study the adsorption capability of CO which is supposed as intermediates for further reduction. Firstly, the CO pulsed adsorption experiment (Figure S7) revealed that the adsorption of CO on the surface of NDSN catalysts could be negligible without an applied electric field, which agreed well with the calculation results.[6b,6c,7] However, the linear polarization test in Ar or CO_2 (Figure S8) suggested that CO could be adsorbed on the surface of NDSN catalysts when there was an electric field. Similar results have been reported on the metal catalysts.[5e,19] Clearly, the different CO adsorption behaviour was caused by the applied electric field. This led us to conduct a cyclic voltammetry (CV) experiment (Figure S9) to investigate the CO adsorption in-situ during the reaction.

As shown in Figure 2a, when the terminal potential in the negative direction was fixed at -0.1175 V *vs* RHE, no CO oxidation peak was found. After the potential was raised to -0.5175 V *vs* RHE, a weakly broad peak at about 0.67 V *vs* RHE was observed. With raising the terminal potential, the peak current at 0.67 V *vs* RHE gradually increased to reach saturation. The peak current at each terminal potential was plotted in Figure 2b. Furthermore, the CO production currents based on the total current (from CV curves in Figure 2a) and FE (Figure S3a) were also presented in Figure 2b. Two valuable conclusions could be drawn: 1) CO can be adsorbed on the surface of NCNT when there was a negatively polarized electric field; 2) with increasing overpotential, the desorption rate would accelerate which implied the low CO binding energy and finally led to a steady adsorption state. Similar results for other NDSN catalysts were shown in supporting information (Figure S10).

The equilibrium potential for the formation of C_xH_y or $C_xH_yO_z$ usually lies in the range of 0.02 V to -0.50 V *vs* RHE (Table S2). However, neither C_xHy nor $C_xH_yO_z$ was observed when NDSN materials were used as catalysts, even if the applied potential was higher than -2.0 V *vs* RHE. Although a considerable amount of CO could be adsorbed on NDSN catalysts with an applied electric field, it cannot be transformed into other carbonaceous products. Thus we supposed that the activation energy was too high to further reduce the adsorbed CO. This was different from the reduction mechanism on the metals (Zn, Au and Ag) discussed above,[17,18] on which the barrier for the reduction of CO to C_xH_y or C_xH_yOz could be overcome by raising the potential (higher than -1.0 V *vs* RHE).[17,18]

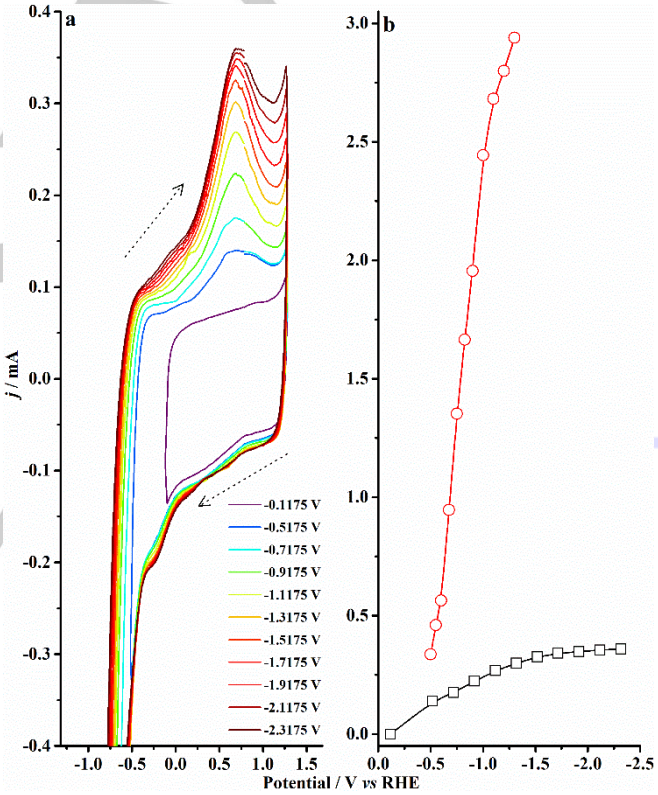

Figure 2. *(a) The CV curves of NCNT-1 catalyst in different potential windows with a scan rate of 20 mV s^{-1} in 0.5 M $NaHCO_3/CO_2$ solution at 25 °C. (b) The peak current of CO oxidation (square), CO production current (circle).*

Combining the above observations, we were able to draw a more explicit mechanism for the CO_2 electro-reduction on NDSN catalysts. The proposed reaction mechanism including two reaction routes was shown in Figure 3. CO_2 reduction was the dominant pathway, which proceeded via an initial rate-determining charge transfer of one electron to CO_2 to form $CO_2^{\bullet-}$, as supported by the Tafel analysis (Figure S5).[5,6,20] $CO_2^{\bullet-}$ can then be reduced to $^*CO$ with the participation of two protons and

another electron. As suggested by the in-situ CO adsorption experiment, the low CO binding energy could result in the release of CO, instead of further being reduced to C_xH_y or $C_xH_yO_z$. The secondary pathway was the reduction of HCO_3^- to HCO_2^-. It should be noted that the terminal proton source should be H_2O (Figure S11). If the CO reduction energy barrier could be overcome with a relatively low potential under which the adsorbed CO would not be completely released and the H_2 evolution reaction should not be promoted to consume all the electrons generated at the anode, further electro-reduction of $^*CO$ to form other carbonaceous products (C_xH_y or $C_xH_yO_z$) could be possible. For instance, the ionic liquid may meet this requirement. Very recently, Han et al. synthesized the nitrogen doped graphene-like materials for the CO_2 electro-reduction catalysts.[21] They found that nitrogen doped carbon catalysts were very efficient for the electrochemical reduction of CO_2 to C_xH_y (CH_4) when using ionic liquid (1-butyl-3-methylimidazolium tetrafluoroborate) as the electrolytes. This results were different from Kumar et al., where they observed that CO_2 was converted to CO over nitrogen doped carbon nanofibers in ionic liquid (1-ethyl-3-methylimidazolium tetrafluoroborate).[6a] Furthermore, these results also proved that the electrolyte had a profound effect on the electrolysis process and consequently changed the product distribution of CO_2 electro-reduction. Therefore, the study of the decisive intermediates responsible for the carbonaceous products of CO_2 electro-reduction is of great importance for the development of CO_2 electro-reduction.

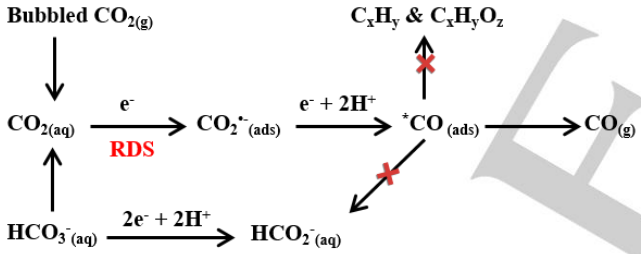

Figure 3. The proposed reaction mechanism on the surface of NDSN materials (RDS: rate determining step).

In summary, the present work exploited the mechanism of CO_2 reduction on NDSN catalysts in $NaHCO_3$ electrolyte to provide a better understanding of the authentic origin of the carbonaceous products (CO and HCO_2^-). Through DEMS and in-situ CO adsorption experiments, we demonstrated that CO was produced from the dissolved CO_2, whereas HCO_2^- came from the reduction of HCO_3^-. Our in-situ CO adsorption experiment provided a clue that the production of other carbonaceous products (C_xH_y or $C_xH_yO_z$) on the sp^2-nanocabron catalysts may be possible if the potential-balance between the CO reduction energy barrier and the CO desorption can be achieved by tuning the surface chemistry of NDSN catalysts or developing a novel electrolyte system.

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Keywords: nitrogen doped sp^2-nanocarbon • carbon dioxide electro-reduction • reaction route • reaction mechanism

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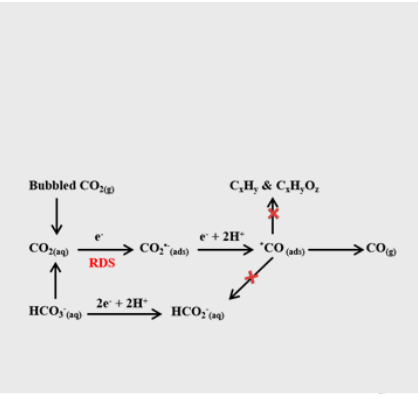
COMMUNICATION

The reaction mechanism on nitrogen doped sp^2-nanocarbon materials is resolved by clarifying the authentic origin of the carbonaceous products: CO and HCO_2^-. Two carbon-reduction pathways are identified: a dominant pathway leading to CO from CO_2 and a secondary pathway leading to HCO_2^- from HCO_3^-. Neither hydrocarbon (C_xH_y), nor alcohol or aldehyde ($C_xH_yO_z$) was detected in the reduction of CO_2.



Junyuan Xu, Bingsen Zhang, Bolun Wang, KuangHsu Wu, Zhangquan Peng, Qingfeng Li, Gabriele Centi, and Dang Sheng Su**

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Decisive intermediates responsible for the carbonaceous products of CO_2 electro-reduction on nitrogen doped sp^2 nanocarbon catalysts in $NaHCO_3$ aqueous electrolyte